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(54) PROCESS FOR THE PRODUCTION OF ELASTOMERIC POLYURETHANE-POLYUREA MOULDED PRODUCTS HAVING A COMPACT SURFACE SKIN

(71) We, BAYER AKTIENGESSELLSCHAFT, a body corporate organised under the laws of Germany, of 509 Leverkusen, Germany; do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a one-step process for the production of elastic mouldings which have a compact surface skin by a technique of reaction injection moulding, using highly reactive systems of polyisocyanates, relatively high molecular weight polyhydroxyl compounds and polyamines.

The production of mouldings having a compact surface skin by the isocyanate polyaddition process is known in principle. It may be carried out, for example, by introducing a reactive and, if desired, also foamable mixture based on compounds having several reactive hydrogen atoms and polyisocyanates into a mould (see, for example, German Auslegeschrift No. 1,196,864). The compounds having reactive hydrogen atoms used are mainly polyethers and polyesters having hydroxyl groups while examples of suitable polyisocyanates include tolylene-2,4- and -2,6-diisocyanates and isomeric mixtures thereof, as well as polyphenylpolymethylene polyisocyanates obtained by a process of aniline-formaldehyde condensation followed by phosgenation. Water and/or fluorochlorinated hydrocarbons, for example, may be used as blowing agents generally cannot be processed by a one-shot process. In these cases, a prepolymer used.

With suitable choice of the starting components (other substances, e.g. chain lengthening agents, such as glycols or diamines, may also be used) it is possible by this process to obtain both elastic products and rigid products, as well as any variations between these extremes.

As will be explained later, systems which contain diamines as chain lengthening agents generally cannot be processed by a one-shot process. In these cases, a prepolymer containing isocyanate groups must first be prepared, and this is then reacted with the diamine in a second step to yield the high molecular weight elastomer (German Auslegeschrift No. 1,240,654).

For moulded products which will be subjected to severe stresses in use, one generally uses only slightly branched starting materials which give rise to products with elastomer-like properties. Mouldings of this type have long been in production on a technical scale (e.g. as shoe soles for the shoe industry). Large mouldings have come into use in the motor car industry.

Processing of the raw materials to produce car body parts is mainly carried out by the so-called "reaction injection moulding process" (RIM). This process involves

a technique of filling the mould by which highly reactive, liquid starting components are injected into the mould within a very short time by means of high output, high pressure dosing apparatus after they have been mixed in so-called "positively controlled mixing heads."

A detailed description of the technology of reaction injection moulding may be found, for example, in the following documents:

Piechota/Röhr: "Integralschaumstoffe", Carl Hanser-Verlag, Munich/Vienna, 1975;

Prepelka/Wharton: "Reaction Injection Moulding in the Automotive Industry", Journal of Cell. Plastics, Vol. II, No. 2, 1975;

Knipp: "Plastics for Automobile Safety Bumpers", Journal of Cell. Plastics, No. 2, 1973;

The reaction injection moulding technique may be used for producing large mouldings weighing from 3 to 10 kg or more, such as the flexible car body parts also known in the motor industry as "soft face elements", i.e. reversibly deformable front and rear parts of motor vehicles.

The following technical advance is achieved by this procedure: large quantities of two liquid, highly reactive starting materials are delivered mechanically within a very short time (generally from 2 to 4 seconds) and mixed at the same time and introduced into a mould in which the mixture is cured to yield the finished product within a time (generally from 1 to 2 minutes) which is also very short for polyurethane materials.

Realisation of this new technology required a solution to the following three problems:

1. In view of the high reactivity of the two starting components (polyisocyanates and compounds which are reactive with polyisocyanates) the reaction mixture must be introduced into the mould within the shortest possible time which at most must not exceed the starting time (i.e. the time required for the reaction to start proceeding). This necessitated the development of highly efficient axial and radial piston pumps which when installed in high pressure machines were capable of delivering at a rate of from 2.5 to 6.5 kg/second. Machines of this type have been described, for example, in German Offenlegungsschrift Nos. 1,778,060 and 2,146,054.

2. Production of a faultless moulding requires not only exact dosing of the two components to keep them at a particular ratio prescribed by the given formulation over the whole period of injection, but also requires intimate mixing of the components from the first to last drop. Perfect mixing is made enormously difficult by the fact that due to their high flow velocities, the two components have only a very short residence time in the mixing chamber of the mixing head. This problem could be solved by using so-called "positively controlled mixing heads" which operate on the principle of "counterflow injection" (see German Auslegeschrift No. 1,948,999 and German Offenlegungsschrift Nos. 2,007,935; 2,219,389 and 2,364,501).

3. When the reaction mixture enters the closed mould, it almost instantly displaces the air contained in it. To ensure that this does not lead to inclusions of air in the reaction mixture and hence faults in the end product, the liquid streaming into the mould must, so to speak, "push" the air forwards in front of it in the form of a "flow front" and expel it through predetermined slots. To ensure complete absence of turbulence during filling of the mould, the material must enter the mould over a wide front along the wall of the mould in a laminar stream. This has been achieved by developing a certain technique of injection through so-called "film gates" described in German Offenlegungsschrift Nos. 2,348,658 and 2,348,608.

It has now surprisingly been found that even extremely highly reactive systems, such as one-shot mixtures of active polyisocyanates, active aromatic polyamines, higher molecular weight polyhydroxyl compounds containing primary hydroxyl groups and strong catalysts may be processed by this method with starting times of less than one second. In these systems, transition from the liquid to solid phase is almost instantaneous so that the liquid reaction mixture solidifies along the walls of the mould.

The most surprising aspect of this method is that, in spite of the short times, it is still possible to fill complicated mould cavities having a large volume and thin walls (wall thickness less than 3 mm). It appears that under these circumstances liquid material is still forced through the space between the solidified surfaces of the moulding on the walls of the mould and fresh material continues to be delivered under the filling pressure of the machine until the end of the filling process. This would explain how it is possible to produce heavier mouldings than would appear to be

mathematically possible from a comparison of the starting time with the filling time (at the given rate of filling per second). In this way the filling time may exceed the starting time by up to 50%.

Solidification of the whole reaction mixture after injection again takes place so rapidly that if highly reactive mixtures are used the mould may be opened after less than 5 seconds to remove the moulded product.

Another decisive advantage of these new systems is that no external mould release agents need be applied to assist removal of product from metal moulds since the end products have self-releasing properties. This is presumably also due to the fact that the reaction mixture undergoes quasi-solidification on the walls of the mould so that it does not wet the walls and there is therefore no reaction between the isocyanate groups and the metal surface.

Due to the extremely rapid solidification of the reaction mixture, only minimum internal mould pressures are produced (less than 2 bar) so that a light construction may advantageously be used for the mould and mould support (only small forces required for keeping the mould closed).

There is no technique other than reaction injection moulding which could conceivably control such reactive systems, i.e. deliver the starting components within the very short times mentioned above, mix them and ensure the production of a perfect moulding which may be removed from the mould after a period of time which is uncommonly short for polyurethanes.

The combination of the novel one-shot system to be described hereinafter with this technology of the reaction injection moulding process therefore has several important advantages over the conventional injection moulding technique in which thermoplastic granulates are moulded by a physical process of melting and resolidification with the application of high temperatures (e.g. from 150 to 200°C) and high pressures (e.g. about 2000 bar) and, in the case of large moulded articles, using enormous machines. These advantages may be enumerated as follows:

1. liquid starting materials, hence
2. the possibility of easy dosing;
3. processing at room temperature;
4. low internal mould pressure (e.g. less than 2 bar);
5. very brief moulding times (e.g. from 5 to 60 seconds, depending on the geometry of the mould) and
6. as a result of 1, 2 and 4, only about 40% of the capital investment required for mechanical equipment.

An object of the present invention is thus a process for the production of an elastomeric polyurethane-polyurea moulding having a compact surface skin which comprises reacting:

- (a) an organic polyisocyanate;
- (b) a compound having a molecular weight of from 1800 to 12,000 and containing at least two primary hydroxyl groups;
- (c) an aromatic polyamine chain lengthening agent;
- (d) a catalyst for the reaction between hydroxyl groups and isocyanate groups; and
- (e) optionally a blowing agent and/or an additive known in polyurethane chemistry;

which process is characterised in that the chain-lengthening agent (c) used in the process is an active as hereinafter defined aromatic diamine or higher polyamine which may be substituted by at least one alkyl group in at least one of the *o*-positions to at least one of the amino groups, optionally together with up to 50%, by weight, based on the said diamine or higher polyamine, of a divalent aliphatic alcohol having two primary hydroxyl groups and in that components (a) to (e) are processed as a one shot system by the reaction injection moulding technique.

According to an earlier proposal by us (German Offenlegungsschrift No. 2,513,817), mixtures of relatively high molecular weight polyhydroxyl compounds, butane-1,4-diol or ethylene glycol as chain-lengthening agent, polyisocyanates and optionally blowing agents are processed to produce moulded articles by the method of the reaction injection moulding process. Compared with the products according to

German Offenlegungsschrift No. 2,513,817, the moulded products produced according to the present invention have distinctly better mechanical properties, in particular the modulus of elasticity depends very little on the temperature (sufficient rigidity in the heat and flexibility at low temperatures).

Although it is known that the elastomeric properties are improved if, in any given system, glycols used as chain-lengthening agents are replaced by aromatic diamines, the one-shot process may then be employed only in exceptional cases, that is to say if very inert diamines are used in which the reactivity of the amino groups towards isocyanates has been greatly reduced by electron attracting substituents. Diamines of this type include, e.g. 3,3'-dichloro-4,4'-diaminodiphenylmethane, *o*-dichlorobenzidine and 2,5-dichloro-1,4-phenylenediamine (British Patent No. 981,935).

As a general rule, but especially in the case of the more reactive polyamines, the components must be reacted together in two or more stages (prepolymer process) on account of the highly differing reactivities of polyols and polyamines towards isocyanates. It was therefore not to be foreseen that it would be at all possible to carry out the one-step process according to the present invention which uses not only polyamines whose reactivity towards isocyanates is not checked, but also very strong catalysts for the polyaddition reaction. It was rather to have been expected that the mixing apparatus would immediately seize-up with polymer product owing to the rapid reaction or that at least the reaction product obtained would be non-homogeneous due to the preferential reaction between polyisocyanates and polyamines. As may be seen from the Examples, however, it is surprisingly found that this is not the case.

The polyisocyanates used as starting components (a) according to the present invention may be aliphatic, cycloaliphatic, araliphatic, aromatic or heterocyclic polyisocyanates, such as those described, for example, by W. Siefken in Justus Liebigs Annalen der Chemie, 562, pages 75 to 136, for example ethylene diisocyanate, tetramethylene-1,4-diisocyanate, hexamethylene-1,6-diisocyanate, dodecane-1,12-diisocyanate, cyclobutane-1,3-diisocyanate, cyclohexane-1,3- and -1,4-diisocyanate and mixtures of these isomers, 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethyl-cyclohexane (DAS No. 1,202,785, US Patent No. 3,401,190), hexahydrotolylene-2,4-diisocyanate, and -2,6-diisocyanate and mixtures of these isomers, hexahydrophenylene-1,3-diisocyanate and/or 1,4-diisocyanate, perhydrodiphenylmethane-2,4'-diisocyanate and/or -4,4'-diisocyanate, phenylene-1,3-diisocyanate and -1,4-diisocyanate, tolylene-2,4-diisocyanate and -2,6-diisocyanate and mixtures of these isomers, diphenylmethane-2,4'-diisocyanate and/or -4,4'-diisocyanate, naphthylene-1,5-diisocyanate, triphenylmethane-4,4',4''-triisocyanate, polyphenyl-polymethylene polyisocyanates which may be obtained by aniline-formaldehyde condensation followed by phosgenation and which have been described, for example, in British Patent Nos. 874,430 and 848,671, *m*- and *p*-isocyanatophenyl-sulphonyl isocyanates according to US Patent No. 3,454,606, perchlorinated aryl polyisocyanates, such as those described, for example in German Auslegeschrift No. 1,157,601 (US Patent No. 3,277,138), polyisocyanates having carbodiimide groups as described in German Patent No. 1,092,007 (US Patent No. 3,152,162), diisocyanates of the type described in US Patent No. 3,492,330, polyisocyanates containing allophanate groups as described, e.g. in British Patent No. 994,890, in Belgian Patent No. 761,626 and in published Dutch Patent Application No. 7,102,524, polyisocyanates containing isocyanurate groups, e.g. as described in US Patent No. 3,001,973, in German Patent Nos. 1,022,789; 1,222,067 and 1,027,394 and in German Offenlegungsschrift Nos. 1,929,034 and 2,004,048, polyisocyanates containing urethane groups as described, e.g. in Belgian Patent No. 752,261 or in US Patent No. 3,394,164, polyisocyanates containing acylated urea groups according to German Patent No. 1,230,778, polyisocyanates containing biuret groups as described, e.g. in German Patent No. 1,101,394 (US Patent Nos. 3,124,605 and 3,201,372) and in British Patent No. 889,050, polyisocyanates prepared by telomerisation reactions as described, for example, in US Patent No. 3,654,106, polyisocyanates having ester groups, such as those mentioned, for example, in British Patent Nos. 965,474 and 1,072,956, in US Patent No. 3,567,763 and in German Patent No. 1,231,688, reaction products of the above-mentioned isocyanates with acetals according to German Patent No. 1,072,385 and polyisocyanates containing polymeric fatty acid groups according to US Patent No. 3,455,883.

Particularly suitable for the process according to the present invention are diisocyanates or polyisocyanates based on 4,4'-diisocyanatodiphenylmethane which are liquid at room temperature. Pure 4,4'-diisocyanatodiphenylmethane (m.p. approx. 40°C) may also be used according to the present invention.

The preferred starting components (a) are liquid polyisocyanates having urethane groups, which may be obtained (e.g. according to German Offenlegungsschrift No. 1,618,380) by reacting 1 mol of 4,4'-diisocyanatodiphenylmethane with from 0.05 to 0.3 mols of low molecular weight diols or triols, preferably with polypropylene glycols having a molecular weight below 700, or diisocyanates having carbodiimide and/or uretioneimine groups based on diphenylmethane diisocyanate, which are obtainable according to German Patent No. 1,092,007 (US Patent No. 3,152,162). Mixtures of the last-mentioned preferred polyisocyanates are also used preferentially. Aliphatic and cycloaliphatic isocyanates are generally less suitable for the purpose of the present invention.

The compounds used as component (b) in the process according to the present invention are preferably polyhydroxy polyalkylene polyethers having at least two primary hydroxyl groups and having molecular weights of from 1800 to 12,000, preferably from 3000 to 7000. Polyethers suitable for the process of the present invention having at least 2, preferably 2 or 3 primary hydroxyl groups are known and may be prepared, e.g. by polymerisation of epoxides, such as ethylene oxide, propylene oxide, butylene oxide, tetrahydrofuran, styrene oxide or epichlorohydrin, either on their own, e.g. in the presence of BF_3 , or by a process of chemical addition of these epoxides, optionally as mixtures or successively, to starting components having reactive hydrogen atoms, such as water, ammonia, alcohols, or amines, e.g. ethylene glycol, propylene glycol-(1,3) or -(1,2), trimethylolpropane, 4,4'-dihydroxy-diphenylpropane, aniline, ethanolamine or ethylene diamine. Sucrose polyethers which have been described, for example, in German Auslegeschrift Nos. 1,176,358 and 1,064,938 may also be used according to the present invention. It is in many cases preferred to use polyethers which contain predominantly primary OH groups (up to 90%, by weight, based on all the OH groups present in the polyether). Polyethers modified with vinyl polymers are also suitable. These may be obtained, for example, by the polymerisation of styrene and acrylonitrile in the presence of polyether (US Patent Nos. 3,383,351; 3,304,273; 3,523,093 and 3,110,695 and German Patent No. 1,152,536). Polybutadienes having OH groups may also be used.

According to the present invention, however, there may also be used polyhydroxyl compounds having at least two primary hydroxyl groups and which contain high molecular weight polyadducts or polycondensates in a finely dispersed form or in solution. Such modified polyhydroxyl compounds are obtained when polyaddition reactions (e.g. reactions between polyisocyanates and amino functional compounds) or polycondensation reactions (e.g. between formaldehyde and phenols and/or amines) are directly carried out *in situ* in the above-mentioned hydroxyl compounds. Processes of this type have been described, for example, in German Auslegeschrift Nos. 1,168,075 and 1,260,142 and in German Offenlegungsschrift Nos. 2,324,134; 2,423,984; 2,512,385; 2,513,815; 2,550,796; 2,550,797; 2,550,833 and 2,550,862. Such polyhydroxyl compounds may also be obtained according to US Patent No. 3,869,413 or German Offenlegungsschrift No. 2,550,860 by mixing an aqueous polymer dispersion with a polyhydroxyl compound and then removing water from the mixture.

According to the present invention, hydroxyl-containing polyesters, polythioethers, polyacetals, polycarbonates or polyester amides containing at least two primary hydroxyl groups of the type known for the production of both homogeneous and cellular polyurethanes may also be used or included. In the case of polyhydroxy-polyesters, these may be used as only component (b) without any polyhydroxy-polyether present.

Suitable polyesters containing primary hydroxyl groups include, e.g. reaction products of polyhydric, preferably dihydric alcohols, optionally with the addition of trihydric alcohols, and polybasic, preferably dibasic carboxylic acids. Instead of free polycarboxylic acids, the corresponding polycarboxylic acid anhydrides or corresponding polycarboxylic acid esters of lower alcohols or mixtures thereof may be used for preparing the polyesters. The polycarboxylic acids may be aliphatic, cycloaliphatic, aromatic and/or heterocyclic and they may be substituted, e.g. by halogen atoms, and/or may be unsaturated.

The following are mentioned as examples: succinic acid, adipic acid, suberic acid, azelaic acid, sebacic acid, phthalic acid, isophthalic acid, trimellitic acid, phthalic acid anhydride, tetrahydrophthalic acid anhydride, hexahydrophthalic acid anhydride, tetrachlorophthalic acid anhydride, endomethylene tetrahydrophthalic acid anhydride, glutaric acid anhydride, maleic acid, maleic acid anhydride, fumaric acid, dimeric and trimeric fatty acids, such as oleic acid, optionally mixed with monomeric fatty acids, dimethyl terephthalate and terephthalic acid-bis-glycol esters. The following are

examples of suitable polyhydric alcohols: ethylene glycol, propylene glycol-(1,2) and -(1,3), butylene glycol-(1,4) and -(2,3), hexanediol-(1,6), octanediol-(1,8), neopentylglycol, cyclohexanedimethanol (1,4-bis-hydroxy-methylcyclohexane), 2-methyl-1,3-propanediol, glycerol, trimethylolpropane, hexanetriol-(1,2,6), butanetriol-(1,2,4), trimethylolmethane, pentaerythritol, quinitol, mannitol and sorbitol, methyl glycoside, diethylene glycol, triethylene glycol, tetraethylene glycol, polyethylene glycols, dipropylene glycol, polypropylene glycols, dibutylene glycol and polybutylene glycols. The polyesters may also contain a proportion of carboxyl end groups. Polyesters of lactones, such as ϵ -caprolactone, or hydroxycarboxylic acids, such as ω -hydroxycaproic acid, may also be used.

Particularly to be mentioned among the polythioethers are the condensation products obtained by reacting thiodiglycol on its own and/or with other glycols, dicarboxylic acids, formaldehyde, aminocarboxylic acids or amino alcohols. The products obtained include polythio mixed ethers, polythio ether esters or polythio ether ester amides, depending on the co-components.

Suitable polyacetals include, for example, the compounds which may be prepared from glycols, such as diethylene glycol, triethylene glycol, 4,4'-dioxethoxy-diphenyldimethylmethane and hexanediol, and formaldehyde. Suitable polyacetals for the purpose of the present invention may also be prepared by the polymerisation of cyclic acetals.

The polycarbonates containing primary hydroxyl groups which may be used may be of the type known, for example those which may be prepared by the reaction of diols, such as propanediol-(1,3), butanediol-(1,4) and/or hexanediol-(1,6), diethylene glycol, triethylene glycol or tetraethylene glycol, with diarylcarbonates, e.g. diphenylcarbonate, or phosgene.

Suitable polyester amides and polyamides include, for example, the predominantly linear condensates prepared from polybasic saturated and unsaturated carboxylic acids or the anhydrides thereof and polyvalent saturated or unsaturated amino alcohols, diamines, polyamines and mixtures thereof.

Representatives of these compounds which may be used according to the present invention have been described, for example, in High Polymers, Vol. XVI, "Polyurethanes, Chemistry and Technology" by Saunders-Frisch, Interscience Publishers, New York, London, Volume I, 1962, pages 32-42 and pages 44-54 and Volume II, 1964, pages 5-6 and 198-199 and in Kunststoff-Handbuch, Volume VII, Vieweg-Höchtlen, Carl-Hanser-Verlag, Munich, 1966, e.g. on pages 45 to 71.

In the process according to the present invention, component (b) preferably consists solely of the classical polyether polyols of polyurethane chemistry having molecular weights of from 1800 to 12,000, preferably from 3000 to 7000, and containing two or most preferably three primary hydroxyl groups. Mixtures of polyethers having two or three primary hydroxyl groups are preferred.

Chain-lengthening agent (c) which is essential to the present invention is any active aromatic diamine or higher polyamine which is preferably liquid or dissolved in the polyol component. By "active" diamines and higher polyamines are meant those whose reactivity towards isocyanates has not been reduced by electron attracting substituents, such as halogen, ester, ether or disulphide, as is the case, for example, with methylene-bis-chloroaniline (Moca, the word "Moca" being a Registered Trade Mark). In principle, it is also possible to use as chain lengthening agent (c) a combination of such diamine or higher polyamine with up to 50% by weight, based on the said amine component of a divalent aliphatic alcohol having two primary hydroxyl groups and optionally ether groups. Chain-lengthening agent (c) is preferably used in the process according to the present invention in quantities of from 5 to 50%, by weight, most preferably from 8 to 35%, by weight, based on component (b).

Aromatic amines which may be used as chain-lengthening agent (c) either alone or as mixtures include, for example, 2,4- and 2,6-diaminotoluene, 2,4'- and/or 4,4'-diaminodiphenylmethane, 1,3- and 1,4-phenylenediamine, naphthylene-1,5-diamine and triphenylmethane-4,4',4''-triamine. There may also be used difunctional or higher polyfunctional aromatic amino compound in which some or all of the amino groups are secondary amino groups, as, for example, in the case of 4,4'-di-(methylamino)-diphenylmethane or 1-methyl-2-methylamino-4-aminobenzene. Liquid mixtures of polyphenyl-polymethylene polyamines of the type obtained by aniline-formaldehyde condensation are also suitable.

Liquid or dissolved aromatic amines which have proved to be particularly suitable for the process according to the present invention are those which contain at least one linear alkyl substituent in the ortho-position to the first amino group and two linear alkyl substituents having from 1 to 3 carbon atoms in the ortho-positions to the

second amino group. Examples include: 1,3-diethyl-2,4-diaminobenzene, 2,4-diaminomesitylene, 1-methyl-3,5-diethyl-2,4-diaminobenzene, 1-methyl-3,5-diethyl-2,6-diaminobenzene, 1,3,5-triethyl-2,6-diaminobenzene and 3,5,3',5'-tetraethyl-4,4'-diaminodiphenylmethane.

The above-mentioned aromatic diamines may, of course, be used as mixtures with each other or in combination with other active aromatic diamines.

It is preferred to use aromatic diamines which have a linear alkyl substituent having from 1 to 3 carbon atoms and in both ortho-positions to each amino group. For processing by the RIM process, it is advantageous that one series of these diamines is liquid at room temperature and miscible with polyhydroxyl compounds in any proportion, particularly with polyhydroxypolyethers. Particularly preferred in this connection is the compound 1-methyl-3,5-diethyl-2,4-diaminobenzene or a mixture of this compound with 1-methyl-3,5-diethyl-2,6-diaminobenzene.

In cases where the diamines used are crystalline at room temperature, they must be dissolved in the polyhydroxyl compounds and the subsequent reaction by the RIM process must, if necessary, be carried out at elevated temperatures (e.g. up to 50°C) for the purpose of reducing the viscosity of the mixture.

Suitable divalent aliphatic alcohols which may be used together with the diamines or higher polyamines as chain-lengthening agents include, e.g. ethylene glycol, tetramethylene glycol, hexamethylene glycol, diethylene glycol or triethylene glycol. Ethylene glycol is preferred.

Catalysts (d), which are also essential to the present invention and without which it is not possible to obtain a moulding which sets rapidly in the mould and has technologically interesting mechanical properties, are preferably organo metallic compounds. According to the present invention, it is preferred to use organo tin compounds, e.g. tin(II) salts of carboxylic acids, such as tin(II) acetate, tin(II) octoate, tin(II) ethyl hexoate or tin(II) laurate, and the dialkyl tin salts of carboxylic acids, such as dibutyl tin diacetate, dibutyl tin dilaurate, dibutyl tin maleate or dioctyl tin diacetate, either alone or preferably as a complex with amidines, such as 2,3-dimethyl-3,4,5,6-tetrahydropyrimidine or 2-methyl-3-cyclohexyl-3,4,5,6-tetrahydropyrimidine, aminopyridines or pyrimidines and hydrazino pyridines or pyrimidines.

Synergistically acting catalyst combinations of this type have been described, for example, in German Offenlegungsschrift Nos. 2,434,185; 2,601,082 and 2,603,834.

Other catalysts which may be used in addition include: known tertiary amines, such as triethylamine, tributylamine, N-methylmorpholine, N-ethylmorpholine, N-cocmorpholine, N,N,N',N'-tetramethyl-ethylenediamine, 1,4-diaza-bicyclo-(2,2,2)-octane, N-methyl-N'-dimethylaminoethyl-piperazine, N,N-dimethylbenzylamine, bis-(N,N-diethylamino-ethyl)-adipate, N,N-diethylbenzylamine, pentamethyl-diethylenetriamine, N,N-dimethylcyclohexylamine, N,N,N',N'-tetramethyl-1,3-butanediamine, N,N-dimethyl-β-phenylethylamine, 1,2-dimethylimidazole and 2-methylimidazole. A preferred catalyst of this type is 1,4-diaza-bicyclo-(2,2,2)-octane.

Tertiary amines having isocyanate-reactive hydrogen atoms include, e.g. triethanolamine, triisopropanolamine, N-methyl-diethanolamine, N-ethyl-diethanolamine, N,N-dimethyl-ethanolamine and reaction products of these compounds with alkylene oxides, such as propylene oxide and/or ethylene oxide.

Silaamines having carbon-silicon bonds as described, e.g. in German Patent No. 1,229,290 may also be used as catalyst, e.g. 2,2,4-trimethyl-2-silamorpholine or 1,3-diethylaminomethyl-tetramethyl-disiloxane.

Basic nitrogen compounds, such as tetra-alkylammonium hydroxides, alkali metal hydroxides such as sodium hydroxide, alkali metal phenolates, such as sodium phenolate, and alkali metal alcoholates, such as sodium methylate, may also be used as catalysts; hexahydrotriazines are also suitable catalysts.

The above-mentioned catalyst may be used alone, e.g. most preferably 1,4-diaza-bicyclo-(2,2,2)-octane, or in combination with organic metal compounds, in particular the organic tin compounds.

Other representatives of catalysts which may be used according to the present invention and details concerning the action of the catalyst may be found in *Kunststoff-Handbuch*, Volume VII, published by Vieweg and Höchsten, Carl Hanser-Verlag, Munich 1966, e.g. on pages 96 to 102.

The catalysts are generally used in a quantity of from 0.01 to 10%, by weight, preferably from 0.05 to 1%, by weight, based on the quantity of compounds (b).

The catalysts to be used according to the present invention should accelerate the polyaddition reaction generally to such an extent that once the starting components have been mixed the reactive mixture has a flow time (time during which the mixture

may still be delivered) of less than seconds, preferably less than 10 seconds and most preferably less than 5 seconds under the operating conditions.

The process according to the present invention is preferably used for producing compact mouldings although blowing agents may also be used, in which case mouldings having a compact surface and cellular interior are obtained. The blowing agents (e) used may be water and/or readily volatile organic substances. Suitable organic blowing agents include, e.g. acetone, ethyl acetate, methanol, ethanol, vinylidene chloride halogen substituted alkanes, such as methylene chloride, chloroform, ethylidene chloride, monofluorotrichloromethane, chlorodifluoromethane or dichlorofluoromethane, or also butane, hexane, heptane or diethyl ether.

The effect of a blowing agent may also be obtained by adding compounds which decompose at temperatures above room temperature to liberate gas, for example, nitrogen, e.g. azo compounds, such as azoisobutyric acid nitrile. Other examples of blowing agents and details concerning the use of blowing agents may be found in *Kunststoff-Handbuch*, Volume VII, published by Vieweg and Höchtlen, Carl Hanser-Verlag, Munich 1966, e.g. on pages 108 and 109, 453 to 455 and 507 to 150.

Surface-active additives (emulsifiers and foam stabilisers) may also be used according to the present invention. Suitable emulsifiers include, e.g. the sodium salts of ricinoleic sulphonates or of fatty acids, or salts of fatty acids with amines, such as oleic acid diethylamine or stearic acid diethanolamine. Alkali metal or ammonium salts of sulphonic acids, such as dodecylbenzene sulphonic acid or dinaphthylmethane disulphonic acid, or of fatty acids, such as ricinoleic acid, or of polymeric fatty acids may also be used as surface active additives.

The foam stabilisers optionally used are mainly water-soluble polyether siloxanes. These compounds generally have a polydimethylsiloxane group attached to a copolymer of ethylene oxide and propylene oxide. Foam stabilisers of this type have been described, for example, in US Patent No. 2,764,565.

Known cell regulators, such as paraffins or fatty alcohols or dimethylpolysiloxanes, pigments, dyes, known flame retarding agents, such as bis-chloroethylphosphate or ammonium phosphate and polyphosphate, stabilisers against ageing and weathering, plasticisers, fungistatic and bacteriostatic substances and fillers, such as barium sulphate, kieselguhr, carbon black or whiting, may also be used according to the present invention.

Other examples of surface active additives, foam stabilisers, cell regulators, stabilisers, flame retarding substances, plasticisers, dyes, fillers and fungistatic and bacteriostatic substances which may be used according to the present invention and details concerning the use and action of these additives may be found in *Kunststoff-Handbook*, Volume VI, published by Vieweg and Höchtlen, Carl Hanser-Verlag, Munich, 1966, e.g. on pages 103 to 113.

The quantity of polyisocyanate (component (a)) used in the process according to the present invention is preferably calculated so that the optionally foamable mixture has an isocyanate index of from 70 to 130, in particular from 90 to 110. By "isocyanate index" is meant the quotient of the number of isocyanate groups and number of groups which are reactive with isocyanates multiplied by 100.

The known reaction injection moulding technique (RIM process) is used for carrying out the process according to the present invention. The quantity of reaction mixture (which is optionally foamable) introduced into the mould is calculated so that the moulded article generally has a density of from 0.8 to 1.2 g/cc, preferably from 0.9 to 1.1 g/cc.

A starting temperature of from 10 to 50°C, preferably from 20 to 30°C, is generally chosen for the mixture introduced into the mould. The temperature of the mould is generally from 40 to 100°C, preferably from 50 to 70°C.

Although the very rapid reaction between components (a) to (e) renders the use of mould release agents superfluous, e.g. for removal of the moulded product from polished metal moulds, the known mould release agents based on wax or silicone may be used if desired. Furthermore, when carrying out the process according to the present invention, the internal mould release agents known in the art, such as those described, for example, in German Offenlegungsschrift Nos. 1,953,637 and 2,121,670, may also be used.

The mouldings obtainable by the process according to the present invention are particularly suitable for the manufacture of flexible car bumpers and car body elements. However, with suitable variation of starting compounds (a) to (e) and particularly if a relatively low proportion of diamine (c) is used, it is also possible to produce, e.g. flexible polyurethane shoe soles which have good abrasion resistance and high mechanical strength.

Examples

Processing of the formulations described in the following Examples was carried out using machines which operate on the counterflow injection principle (HK machines⁽¹⁾).

For the mechanical tests, plates measuring 120×20×0.4 cm were prepared in a steel plate mould which could be tempered. The mould was filled from the long side through a sprue gate.

The present invention is not restricted to the machines mentioned above, but the mixing apparatus used must have a high output capacity (generally more than 0.5 kg/sec., preferably 1 kg/sec. for a moulded article weighing 1 kg.) so that the extremely reactive liquid reaction mixture may be introduced into the mould within the shortest possible time.

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Example 1

83.50 parts by weight, of a polyether having OH number 28 obtained by addition of propylene oxide and subsequent addition of ethylene oxide to trimethylolpropane;

12.50 parts, by weight, of a mixture of 65 parts, by weight, of 1-methyl-3,5-diethylphenylene-2,4-diamine and 35 parts, by weight, of 1-methyl-3,5-diethylphenylene-2,6-diamine;

0.05 parts by weight, of a complex of 1 mol of dibutyl tin dilaurate and 1 mol of 2,3-dimethyl-3,4,5,6-tetrahydropyrimidine; and

4.00 parts, by weight, of monofluorotrichloromethane;

were combined to form a polyol component and processed with 33.50 parts, by weight, of a reaction product of tripropylene glycol and 4,4'-diphenylmethane diisocyanate (23%, by weight, NCO) by the RIM process.

The temperature of the raw materials was 25°C and the temperature of the plate mould was adjusted to 50°C. The setting time in the mould was 30 seconds.

The polyurethane-polyurea elastomer obtained was tempered at 120°C for one hour. The following mechanical properties were determined on the test plate (values obtained using an untempered plate are also shown for comparison).

		Tempered	Untempered	
	Unit Weight (kg/m ³)	1062	1076 (DIN 53420)	
	Tensile strength (MPa)	17.0	17.3 (DIN 53504)	
35	Elongation at break (%)	+65°C 412	356	35
		(RT) 391	374 (DIN 53504)	
	Room temperature	-30°C 307	258	
	Tear propagation resistance without incision (kN/m)	83	80 (DIN 53515)	
40	Tensile strain at 50% elongation (MPa)	5.04	5.28 (DIN 53504)	40
	Shore A hardness	93	94 (DIN 53505)	
	E-modulus, dynam. (MPa)			
	(after Roelig)			
		+65°C 59.6	64.2	
45		RT 90.8	101	45
		-30°C 243	309	

Example 2

100.00 parts, by weight, of the polyol mixture from Example 1 were processed by the RIM process with 24.00 parts, by weight, of a mixture of two polyisocyanates having an isocyanate content of 32.5%, by weight. The mixture of polyisocyanates has the following composition:

30.00 parts, by weight, of a partially carbodiimised 4,4'-diphenylmethane diisocyanate having an isocyanate content of 30%, by weight; and

70.00 parts, by weight, of pure 4,4'-diphenylmethane diisocyanate.

The processing conditions employed were the same as in Example 1. The following mechanical properties were then determined on the test plate:

	Unit weight (kg/cm ³)	1015	
	Tensile strength (MPa)	12.5	
60	Elongation at break (%) +65°C	439	60
	RT	399	
	-30°C	364	

	Tear propagation resistance without incision (kN/m)	60	
	Tensile stress at 50% elongation (MPa)	3.3	
5	Shore A hardness	84	
	E-modulus (MPa) +65°C	36.9	5
	RT	48.7	
	-30°C	113	

Example 3

10	77.00 parts, by weight, of a polyether having OH number 28 which had been obtained by addition of propylene oxide followed by addition of ethylene oxide to trimethylol propane;	10
	23.00 parts, by weight, of a mixture of 65 parts, by weight, of 1-methyl-3,5-diethyl-phenylenediamine-(2,4) and	
15	35 parts, by weight, of 1-methyl-3,5-diethylphenylenediamine-(2,6); and	15
	0.10 parts, by weight, of dibutyl tin dilaurate;	
20	were combined to form a polyol component which was then processed with 55.00 parts, by weight, of a reaction product of tripropylene glycol and 4,4-diphenylmethane diisocyanate (23%, by weight, NCO) by the RIM process. The processing conditions employed were the same as in Example 1. The following mechanical properties were determined on the test plate:	20

	Unit weight (kg/m ³)	1091	
	Tensile strength (MPa)	31.0	
	Elongation at break (%) +65°C	316	
25	RT	290	
	-30°C	222	25
	Tear propagation resistance without incision(kN/m)	155	
	Tensile stress at 50% elongation (MPa)	15.4	
30	Shore D hardness	62	
	E-modulus (MPa) +65°C	283	30
	RT	449	
	-30°C	977	

Example 4

35	83.50 parts, by weight, of a polymer polyol having OH number 28 which had been prepared by graft copolymerisation of 20 parts, by weight, of styrene/acrylonitrile (proportion, by weight, 40:60) in 80 parts, by weight, of a propylene oxide-ethylene oxide mixed polyether (OH number 34) which had been started on trimethylolpropane;	35
40	12.50 parts, by weight, of a mixture of 65 parts, by weight, of 1-methyl-3,5-diethyl-phenylenediamine-(2,4) and	40
	35 parts, by weight, of 1-methyl-3,5-diethylphenylene diamine-(2,6);	
	0.05 parts, by weight, of a complex of 1 mol of dibutyl tin dilaurate and 1 mol of 2,3-dimethyl-3,4,5,6-tetrahydropyrimidine; and	
45	4.00 parts, by weight, of monofluorotrichloromethane;	45
	are combined to form a polyol component and processed by the RIM process with 33.50 parts, by weight, of a reaction product of tripropylene glycol and 4,4'-diphenylmethane diisocyanate which had an isocyanate content of 23%, by weight.	
	The same processing conditions were chosen as in Example 1. The following mechanical properties were determined on the test plate:	

50	Unit weight (kg/m ³)	1009	50
	Tensile strength (MPa)	14.6	
	Elongation at break (%) +65°C	379	
	RT	369	
55	-30°C	202	
	Tear propagation resistance without incision (kN/m)	71	55
	Tensile strength at 50% elongation (MPa)	5.4	
	Shore A hardness	92	
60	E-modulus (MPa) +65°C	62	
	RT	129	60
	-30°C	516	

Example 5

100.00 parts, by weight, of the polyol mixture from Example 3 were processed by the RIM process with

5 41.00 parts, by weight, of a polyisocyanate which had been obtained by phosgenating aniline-formaldehyde condensates and which had a viscosity of 320 cP at 25°C and an isocyanate content of 31.5%, by weight. 5

The processing conditions employed were the same as in Example 1. The polyurethane-polyurea-elastomer obtained was tempered at 120°C for one hour. The following mechanical properties were then determined on the test plate:

10	Unit weight (kg/m ³)	1048	10
	Tensile strength (MPa)	18.1	
	Elongation at break (%) +65°C	174	
	RT	210	
	-30°C	159	
15	Tear propagation resistance without incision (kN/m)	90	15
	Tensile stress at 50% elongation (MPa) +65°C	9.07	
	RT	11.8	
	-30°C	20.3	
20	Shore D hardness	56	20

Example 6

60.00 parts, by weight, of a polyether having OH number 28 which had been obtained by addition of propylene oxide followed by addition of ethylene oxide to propylene glycol;

25 17.00 parts, by weight, of a polyether having OH number 35 which had been obtained by addition of propylene oxide followed by addition of ethylene oxide to trimethylol propane; 25

23.00 parts, by weight, of a mixture of 65 parts, by weight, of 1-methyl-3,5-diethylphenylenediamine-(2,4) and

30 35 parts, by weight, of 1-methyl-3,5-diethylphenylenediamine-(2,6); and 30

0.60 parts, by weight, of 1,4-diaza-bicyclo-(2,2,2)-octane;

were combined to form a polyol component and processed by the RIM process with 45.50 parts, by weight, of a polyisocyanate which had been obtained by phosgenation of aniline-formaldehyde condensates followed by reaction with a diol having an OH number of 580, which polyisocyanate had a viscosity at 25°C of 430 cP and an isocyanate content of 28%, by weight.

The processing conditions employed were the same as in Example 1. The polyurethane-polyurea elastomer obtained was tempered at 120°C for one hour. The following mechanical properties were then determined on the test plate:

40	Unit weight (kg/m ³)	1087	40
	Tensile strength (MPa)	21.9	
	Elongation at break (%) +65°C	249	
	RT	313	
	-30°C	188	
45	Tear propagation resistance without incision (kN/m)	110	45
	Tensile strength at 50% elongation (MPa) +65°C	9.62	
	RT	12.5	
	-30°C	22.2	
50	Shore D hardness	61	50

Example 7

7.60 parts, by weight, of 4,4'-diamino-diphenylmethane were dissolved at 60°C in

55 92.30 parts, by weight, of a polyether having OH number 28 which had been obtained by addition of propylene oxide followed by addition of ethylene oxide to trimethylol propane and the solution was combined with 55

0.10 parts, by weight, of a complex of 1 mol of dibutyl tin dilaurate and 1 mol of 2,3-dimethyl-3,4,5,6-tetrahydropyrimidine to form a polyol component which was processed with

23.60 parts, by weight, of a reaction product of tripropylene glycol and 4,4'-diphenylmethane diisocyanate (23%, by weight, NCO) by the RIM process.

The temperature of the raw materials was 30°C and the temperature of the plate mould was adjusted to 50°C. The setting time in the mould was 30 seconds.

The polyurethane-polyurea elastomer obtained was tempered at 120°C for one hour. The following mechanical properties were determined on the test plate:

Unit weight (kg/m ³)	1099
Tensile strength (MPa)	8.53
Elongation at break (%) +65°C	321
RT	369
-30°C	338
Tear propagation resistance without incision (kN/m)	67
Tensile stress at 50% elongation +65°C	3.61
RT	369
-30°C	9.37
Shore A hardness	90

Example 8

9.50 parts, by weight, of 2,4'-diamino-diphenylmethane were dissolved at 60°C in

90.40 parts, by weight, of a polyether having OH number 28 which had been obtained by addition of propylene oxide followed by addition of ethylene oxide to trimethylol propane and the solution was combined with

0.10 parts, by weight, of a complex of 1 mol of dibutyl tin dilaurate and 1 mol of 2,3-dimethyl-3,4,5,6-tetrahydropyrimidine to form a polyol component which was processed with

23.60 parts, by weight, of a reaction product of tripropylene glycol and 4,4'-diphenylmethane diisocyanate (23%, by weight, NCO) by the RIM process.

The temperature of the raw materials was 30°C and the temperature of the mould was adjusted to 50°C. The setting time in the mould was 30 seconds.

The polyurethane polyurea elastomer obtained was tempered at 120°C for one hour. The following mechanical properties were determined on the test plate:

Unit weight (kg/m ³)	1102
Tensile strength (MPa)	16.9
Elongation at break (%) +65°C	332
RT	381
-30°C	315
Tear propagation resistance without incision (kN/m)	75
Tensile stress at 50% elongation +65°C	2.61
RT	3.45
-30°C	8.41
Shore A hardness	84

Example 9

77.00 parts, by weight, of a polymer polyol having OH number 28 prepared by graft polymerisation of styrene and acrylonitrile (proportions, by weight 40:60) on a poly-(oxypropylene)triol which has been tipped with ethylene oxide having a molecular weight of 4800;

23.00 parts, by weight, of a mixture of 65 parts, by weight, of 1-methyl-3,5-diethyl-phenylenediamine-(2,4) and

35 parts, by weight, of 1-methyl-3,5-diethylphenylenediamine-(2,6); and

0.20 parts, by weight, of a complex of 1 mol of dibutyl tin dilaurate and 1 mol of 2,3-dimethyl-3,4,5,6-tetrahydropyrimidine;

were combined to form a polyol component which was processed with 55.00 parts, by weight, of a reaction product of tripropylene glycol and 4,4'-diphenylmethane diisocyanate (isocyanate content 23%) by the RIM process.

The processing conditions employed were the same as in Example 1. The very rigid polyurethane-polyurea elastomer obtained was tempered at 120°C for one hour.

The following mechanical properties were then determined on the test plate:

	Unit weight (kg/m ³)	1105	
	Tensile strength (MPa)	38	
5	Elongation at break (%) +65°C	329	
	RT	329	5
	-30°C	~108	
	Tear propagation resistance without incision (kN/m)	163	
10	Tensile strength at 50% elongation (MPa) +65°C	13.4	
	RT	19.0	10
	-30°C	44.5	
	Shore D hardness	68	

Example 10

In this and the following Examples, the mould is heated to 50°C. The polyol component is heated to 50°C and the isocyanate component is heated to 40°C. The mould time is 30 seconds. The resulting elastomeric mouldings are tempered for 1 hour at 120°C.

100 parts, by weight, of a linear polyester having an OH number of 55, which was obtained by condensation of adipic acid with ethylene glycol and tetramethylene glycol, 30 parts, by weight, of a mixture consisting of 65 parts, by weight, of 1-methyl-3,5-diethyl-phenylenediamine-(2,4) and 35 parts, by weight, of 1-methyl-3,5-diethyl-phenylene-diamine-(2,6) and 0.2 parts, by weight, of a complex of one mol of dibutyl tin dilaurate and one mol of 2,3-dimethyl-3,4,5,6-tetrahydropyrimidine are mixed to form a polyol component. This polyol component is processed by the RIM process with the reaction product of tripropylene glycol and 4,4'-diisocyanato diphenylmethane (23%, by weight, of NCO) using a weight ratio polyol:polyisocyanate of 100:61.5.

The following mechanical properties were then determined on the test plate:

	Unit weight (kg/m ³)	1180	
30	Tensile strength (MPa)	36.1	30
	Elongation at break (%)	243	
	Tear propagation resistance with incision (kN/m)	167	
35	Shore D hardness	68	35

Example 11

As described in Example 10, 100 parts, by weight, of the polyol component are processed with 51 parts, by weight, of a polyisocyanate component. This polyisocyanate component had been prepared by phosgenation of an aniline-formaldehyde condensate and subsequent reaction of the phosgenation product with a diol having an OH-number of 580 so that the resulting product had a viscosity at 25°C of 430 cP and an NCO-content of 28%, by weight.

The following mechanical properties were then determined:

	Unit weight (kg/cm ³)	1179	
45	Tensile strength (MPa)	37.3	45
	Elongation at break (%)	224	
	Tear propagation resistance without incision (kN/m)	115	
	Shore D	68	

Example 12

100 parts, by weight, of the polyester of Example 10, 10 parts, by weight, of the diamine mixture of Example 10 and 0.2 parts, by weight, of the complex of Example 10 are mixed to form a polyol component. This polyol component is processed in combination with the reaction product of 4,4'-diisocyanatodiphenylmethane with tripropylene glycol (23%, by weight, of NCO). The weight ratio polyol:polyisocyanate was 100:35.5.

The following mechanical properties were then determined

	Unit weight (kg/m ³)	1122	
60	Tensile strength (MPa)	30.3	60
	Elongation at break (%)	224	
	Tear propagation resistance with incision (kN/m)	65.2	
	Shore D	38	

Example 13

100 parts, by weight, of the polyester of Example 10, 20 parts, by weight, of the diamine mixture of Example 10, 10 parts, by weight, of ethylene glycol and 0.2 parts, by weight, of the complex of Example 10 are mixed to form a polyol component. This polyol component is reacted following the procedure of Example 10 with the polyisocyanate component of Example 12 (weight ratio polyol:polyisocyanate=100:91.5).

The following mechanical properties were then determined:

	Unit weight (kg/m ³)	1205	
	Tensile strength (MPa)	54.6	
10	Elongation at break (%)	292	10
	Tear propagation resistance with incision (kN/m)	178	
	Shore D	70	

WHAT WE CLAIM IS:—

1. A process for the production of an elastomeric polyurethane-polyurea moulded product having a compact surface skin which comprises reacting, as a one-shot system by the reaction injection moulding technique:
 - (a) an organic polyisocyanate;
 - (b) a compound having a molecular weight of from 1800 to 12,000 and containing at least two primary hydroxyl groups;
 - (c) as chain-lengthening agent, an active as hereinbefore defined aromatic diamine or higher polyamine which may be substituted by at least one alkyl group in at least one of the ortho-positions to at least one of the amino groups;
 - (d) a catalyst for the NCO/OH reaction; and, optionally,
 - (e) a blowing agent and/or a conventional additive.
2. A process as claimed in claim 1 in which component (c) additionally comprises up to 50%, by weight, based on the amine component, of a divalent aliphatic alcohol having two primary hydroxyl groups.
3. A process as claimed in claim 1 or claim 2 in which component (c) is either liquid or is dissolved in the polyol component.
4. A process as claimed in any of claims 1 to 3 in which component (c) comprises an active aromatic diamine having at least one linear alkyl substituent in the ortho-position to one amino group and two linear alkyl substituents each having from 1 to 3 carbon atoms in the ortho-positions to the other amino group.
5. A process as claimed in any of claims 1 to 4 in which component (c) comprises 1-methyl-3,5-diethyl-2,4-diaminobenzene and/or 1-methyl-3,5-diethyl-2,6-diaminobenzene.
6. A process as claimed in any of claims 1 to 5 in which component (c) is used in an amount of from 5 to 50%, by weight, based on the weight of component (b), and the amount of component (a) used is calculated so that the reaction mixture has an isocyanate index of from 70 to 130.
7. A process as claimed in any of claims 1 to 6 in which component (b) contains three primary hydroxyl groups.
8. A process as claimed in claim 1 substantially as herein described.
9. A process as claimed in claim 1 substantially as herein described with reference to any one of the Examples.
10. An elastomeric polyurethane-polyurea moulded product when produced by a process as claimed in any of claims 1 to 9.

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